

Behavior of Arsenic and Other Redox-Sensitive Elements in Crowley Lake, CA: A Reservoir in the Los Angeles Aqueduct System

PENELOPE E. KNEEBONE AND
JANET G. HERING*

*Environmental Engineering Science (138-78), California
Institute of Technology, 1200 East California Boulevard,
Pasadena, California 91125*

Elevated arsenic concentrations in Crowley Lake derive from upstream geothermal inputs. We examined the water column of Crowley Lake under stratified and unstratified conditions, seeking evidence for algal uptake and transformation of arsenic and its deposition to and release from the sediments. Vertical profiles of other elements, which might either influence or track the cycling of arsenic, were also examined. Manganese and phosphorus concentrations increased with depth below the oxycline under stratified conditions, consistent with a sediment source of these elements. However, these elements did not accumulate in the hypolimnion during the period of stratification. This can be explained by accounting for the dynamics of reservoir operation in which water withdrawn from the hypolimnion is replaced from the epilimnion or surface inflows. Depletion of phosphorus in the surface water was incomplete during stratification, suggesting that phosphorus is not a limiting nutrient. Vertical profiles of total arsenic during stratification did not provide evidence for release of arsenic from the sediment; concentrations were either uniform with depth or showed a mid-depth minimum at the oxycline attributable to internal recycling within the water column. There was neither depletion of arsenic nor evidence for methylated arsenic species in the productive surface water. Arsenic was present as arsenate in the epilimnion and as a mixture of arsenate and arsenite in the hypolimnion. In the absence of an efficient mechanism to transport arsenic from the water column to the sediments, the substantial mass flux of arsenic through Crowley Lake results in only a moderate accumulation of arsenic in the sediments. Arsenic in the sediments appears to be sequestered by sulfide phases, thus release of arsenic from Crowley Lake sediments should not constitute a threat to the water quality of the Los Angeles Aqueduct.

Introduction

Elevated arsenic concentrations in Crowley Lake derive from geothermal springs in Hot Creek, an indirect tributary. These springs are the major source of arsenic to Crowley Lake, which is the first reservoir in the Los Angeles Aqueduct (LAA) system (1). The LAA provides up to 75% of the water supply for the City of Los Angeles, serving a population of ap-

proximately 3.2 million people. The historical annual average arsenic concentration in water delivered to the LAA Filtration Plant in Sylmar, CA, is 20 ppb ($0.3 \mu\text{M}$), which is below the current standard of 50 ppb ($0.7 \mu\text{M}$) but substantially above the standard of 5 ppb ($0.07 \mu\text{M}$) proposed by the U.S. Environmental Protection Agency in May 2000; the final rule is due to be promulgated in January 2001 (2).

To meet the ocean water discharge standard for arsenic (12 ppb, $0.16 \mu\text{M}$), the LAA water supply is currently being treated by the addition of ferric chloride and polymer at the Cottonwood Treatment Plant, located 220 km south of Crowley Lake. The arsenic-bearing floc is subsequently deposited in Haiwee Reservoir, 27 km south of the treatment plant. Although this is a viable interim strategy, the long-term sequestration of arsenic in this sediment is uncertain (3).

The springs in Hot Creek constitute a relatively localized source of arsenic, and the total flow of Hot Creek is only 4–10% of the total flow at the LAA Filtration Plant. Thus, treatment for arsenic removal at Hot Creek could be a viable strategy for meeting the anticipated drinking water standard. The effectiveness of this treatment would be compromised if the resulting change in water conditions led to release of arsenic stored in the sediments of Crowley Lake.

Arsenic accumulates in lake sediments via processes that transfer arsenic from the water column to particulate material which is then deposited to the lake floor. These processes include sorption to manganese and/or iron oxyhydroxides and uptake by phytoplankton with incorporation into algal biomass (4–6). Crowley Lake sediments have moderately elevated arsenic concentrations, ranging from 4 to 80 mg/kg with an average of 30 mg/kg (7).

The surface waters of Crowley Lake are very productive because of large inputs of geothermally derived phosphate (7–9). Algal uptake of arsenate, which is chemically similar to phosphate, has been identified based on "nutrient-like" arsenic profiles (4, 6). Occurrence of the methylated species monomethylarsonate (MMA) and dimethylarsenate (DMA) and of the reduced inorganic species arsenite in oxygenated surface waters is indicative of algal transformation of arsenic (5, 6, 10, 11). The methylated species are believed to be detoxification products (12, 13).

Arsenic deposited to sediments can be either immobilized and buried or partially remobilized into the overlying water. Arsenic incorporated in algal biomass will be released upon remineralization of the biomass but may be subsequently immobilized, either by sorption onto metal oxyhydroxides in oxic sediments or by incorporation into sulfide solids in anoxic sediments (14, 15). The concentration of dissolved arsenic in pore waters, and hence available for transport to the overlying water, can be controlled by the solubility of sulfide minerals in sulfidic environments (16). However, arsenic is usually more mobile under reducing conditions than under oxidizing conditions because of the strong tendency of arsenic to sorb to, and hence be immobilized by, iron and manganese oxyhydroxides, which persist only under oxidizing conditions.

Remineralization of organic matter and reductive dissolution of iron and manganese oxyhydroxides in anoxic sediments result in characteristic water column profiles for nutrient and redox-active elements in lakes under stratified conditions (4, 14, 17, 18). In this study, profiles of manganese, iron, phosphorus, and arsenic in the water column of Crowley Lake were obtained under stratified and unstratified conditions and were examined to determine the potential for release of arsenic from Crowley Lake sediments.

* Correspondence author telephone: (626)395-3644; fax: (626)-395-2940; e-mail: jhering@caltech.edu.

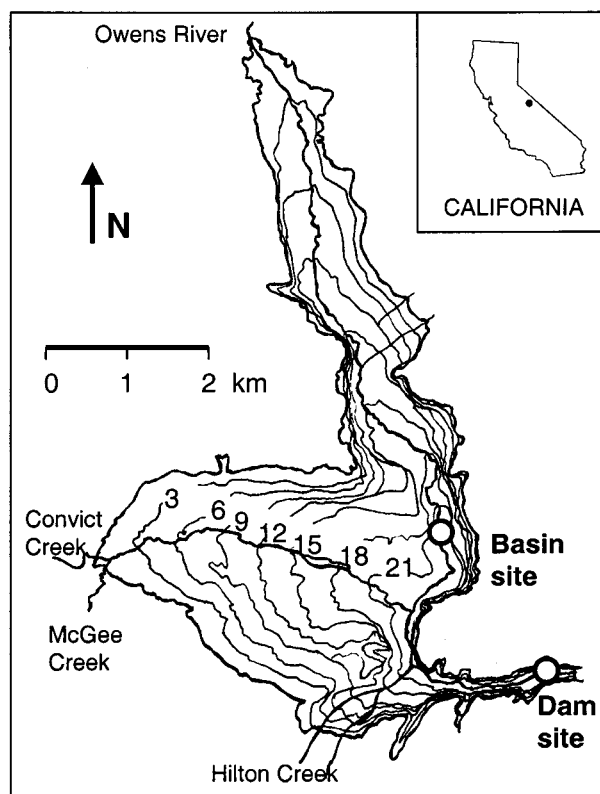


FIGURE 1. Bathymetric map of Crowley Lake with sampling sites marked. Isoclines in meters. Data provided by Crowley Lake Fish Camp.

Experimental Procedure

Sample Collection. The water column of Crowley Lake was sampled at two sites on August 5, 1998; September 3, 1998; and May 11, 1999. The reservoir stage was 2066 m on August 4, 1998, and 2065 m on September 16, 1998 (19). On the basis of month-end storage (20), the elevation on May 11, 1999, was estimated to be 2063 m. One site (the deepest part of the lake) was on the dam arm, approximately 150 m from the dam ($37^{\circ}35'17.3''$ N, $118^{\circ}42'40.7''$ W, hereafter referred to as "dam site"); the second site was in the main basin, near the chalk cliffs of the east bank ($37^{\circ}35'46.8''$ N, $118^{\circ}43'49.8''$ W, hereafter referred to as "basin site"; Figure 1). The dam site position was fixed by tying up to a permanent buoy line whereas the basin site position was prone to wind-driven drift on the order of 30 m southeastward during the period of sample collection on each sampling date.

A peristaltic pump was used to draw water from each depth with flow directed through a cell equipped with dissolved oxygen and combined pH/temperature electrodes (Orion, model 1230 multimeter). When dissolved oxygen and pH readings stabilized, the flow was diverted for collection of 1-L samples in HDPE bottles. Samples with low oxygen content were collected in cubitainers flushed with nitrogen to minimize contact with air. All laboratory and field vessels were soaked for 24 h in 10% (v/v) HCl and triple rinsed in 18 M Ω ·cm (Millipore Milli-Q UV Plus system) water before use.

Sample Processing. Bulk samples were processed within 8 h of collection and stored on ice before and after processing. Filtered and unfiltered aliquots were taken for anion and metal analyses. Filtered samples were obtained using syringe-tip filter units (Nucleopore) holding 0.45- μ m cellulose nitrate membranes (Sartorius).

For determination of arsenic speciation, 100 mL of sample was acidified (to pH \sim 4) and passed through anion exchange

columns as described by Wilkie and Hering (21). Arsenate ($pK_{a1} = 2.2$, $pK_{a2} = 7.0$) is retained on the column, and arsenite ($pK_{a1} = 9.1$) passes through the column and is measured in the effluent. Standard additions of DMA (Sigma Aldrich) and MMA (ChemService) to water samples collected from Hot Creek confirmed that, in this sample processing, DMA ($pK_a = 6.3$) passes through and MMA ($pK_a = 2.6$) is retained on the anion exchange columns.

Deionized water blanks were processed at the same time as samples. Samples for arsenic, phosphorus, iron, and manganese analysis were acidified to 1% (v/v) nitric acid.

Analysis. Arsenic, iron, manganese, and phosphorus were quantified by inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer/Sciex Elan 5000A system). An arsenic stock solution (0.0130 M) was prepared from sodium arsenate; a phosphorus stock solution (0.0100 M) was prepared from monosodium phosphate. Iron and manganese stocks (1.00 g L $^{-1}$) were obtained commercially (VWR Scientific). Calibration standards were prepared immediately prior to each analysis by dilution of the stocks. All chemicals were reagent grade or better and were used without further purification.

Direct determination of MMA in samples collected in September 1998 was performed using ion chromatography (IC, Dionex DX500 with an IonPac AG11 4 mm guard column and IonPac AS11 4 mm analytical column) coupled with ICP-MS (Hewlett-Packard 4500 system). Arsenic concentrations of 0.015 μ M could be detected using this method. Conductivity was measured in unacidified subsamples (Orion, model 1230 multimeter).

Results and Discussion

General Site Characteristics. The dissolved oxygen profiles for August and September show a pronounced oxycline with negligible dissolved oxygen below 12 m at the dam site and below 10 m at the basin site (Figure 2A,D). In May this stratification is almost completely broken down, with slight oxygen depletion in the near-bottom water. These patterns are consistent with the records of long-term monthly monitoring conducted by the LA Department of Water and Power (LADWP), which show that anoxic conditions in the hypolimnion develop in the summer months (19).

Thermal stratification is not strong in August or September (Figure 2C,F). Temperature differences between surface and bottom waters were 4.9 (dam site) and 4.4 $^{\circ}$ C (basin site) in August and 3.3 (dam site) and 2.5 $^{\circ}$ C (basin site) in September. These measurements are consistent with the 2.8 $^{\circ}$ C temperature difference between surface and bottom waters measured on September 16 by the LADWP when dissolved oxygen was still undetectable in the bottom waters (19).

The high pH in the epilimnion in both August and September (Figure 2B,E) reflects the intense productivity during the summer months. Large flocs of phytoplankton were observed floating in the surface water at these times. These flocs were absent in May. An algal assay conducted in early June 1975 suggested that Crowley Lake was nitrogen limited (8). An independent study of chlorophyll *a* in Crowley Lake in 1982 showed evidence for high algal biomass and revealed nitrogen-to-phosphorus sestonic ratios below 22 and estimated loading ratios as low as 7, indicative of a lack of phosphorus limitation (9). The major sources of phosphorus to Crowley Lake are Big Springs (on the Owens River above its convergence with Hot Creek) and Hot Creek, evidenced by soluble reactive phosphorus in the Owens River increasing from 1.7 μ M above Big Springs to 6.4 μ M below this source and decreasing from 4.2 μ M in Lower Hot Creek to 4.1 μ M in the Owens River below Hot Creek (9). These phosphorus inputs make Crowley Lake unusual, as most lakes in which arsenic cycling has been studied are phosphorus limited.

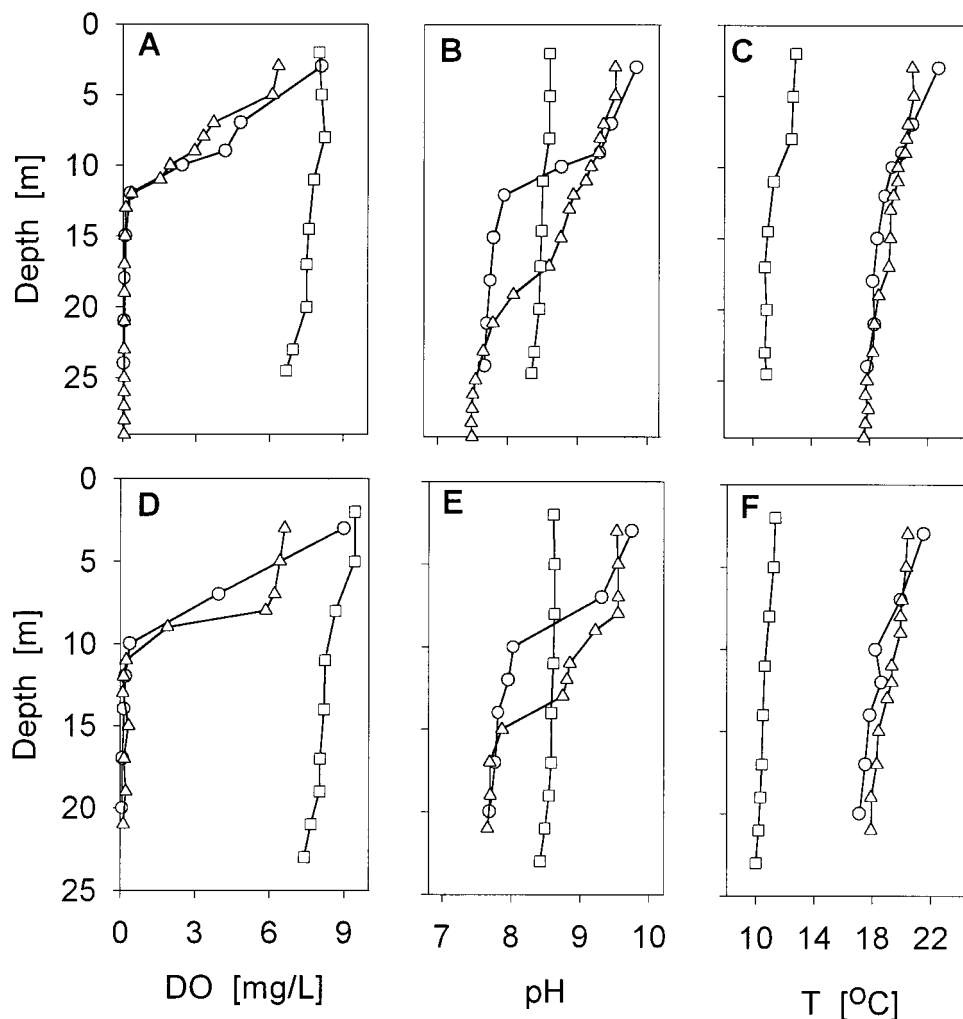


FIGURE 2. Water quality parameters measured at Crowley Lake dam site (A–C) and basin site (D–F) as a function of depth. Symbols: (○) August 4, 1998; (△) September 3, 1998; (□) May 11, 1999.

Conductivity increases gradually from ~ 270 to $\sim 320 \mu\text{S cm}^{-1}$ from the surface to the bottom at both sites in August and September with the exception of a dip in conductivity (to $\sim 200 \mu\text{S cm}^{-1}$) at 10 m at the dam site in August (data not shown).

Crowley Lake is also unusual in terms of its bathymetry and hydrology. Impounded in 1939, the reservoir consists of a broad, shallow basin with a deep channel along the eastern side following the old Owens River (Figure 1). The volume of the hypolimnion is approximately 30% of the total lake volume. The reservoir outflow is regulated by the LADWP and varies dramatically on a daily, weekly, and monthly basis. Residence times, calculated as month-end storage divided by total monthly outflow, varied from 0.3 to 6.7 yr in 1998. Since the dam outlet is located approximately 21 m below the surface, water is withdrawn from the hypolimnion; therefore, the chemical profile development typically observed as stratification intensifies in a lake with an isolated hypolimnion is likely to be significantly perturbed in Crowley Lake.

Manganese—Significant Release from Sediment under Stratified Conditions. The manganese profiles under stratified conditions show a strong increase in the bottom waters (Figure 3A,D). Comparison of the dissolved oxygen and manganese profiles suggests that reduced manganese diffuses upward from the sediment and is oxidized upon reaching the oxycline. A black precipitate was observed in the sample collected from a depth of 12 m at the dam site in August.

Dissolution of this precipitate with hydroxylamine hydrochloride (0.04 M) in acetic acid (25% v/v) and analysis of the leachate by ICMPS indicated that it contained arsenic, iron, and manganese. Although this was a partial digestion, molar ratios of As:Fe and As:Mn were 1:3 and 1:9, respectively (22). This feature was not captured in the unfiltered profile as the precipitate settled rapidly in the collection vessel and was not transferred to the subsample taken for analysis. No precipitates were observed at the basin site in August or at either site in September, suggesting that these precipitates are a highly localized or transient feature.

Throughout the water column in August and in the bottom waters in September, filtered and unfiltered manganese concentrations were the same within experimental error. However, in the upper 12 m at both sites in September and throughout the water column in May (when the entire water column was well-oxygenated), filtered manganese concentrations were only 10–50% of the unfiltered values.

The manganese profiles at the basin site were roughly comparable in August and September whereas, at the dam site, manganese concentrations were consistently lower in September than in August. This is contrary to the increase in manganese concentration that would be expected in an isolated hypolimnion over a period of stratification. However, the hypolimnion of Crowley Lake is not isolated, and the dynamics of reservoir operation can be expected to affect accumulation in the hypolimnion.

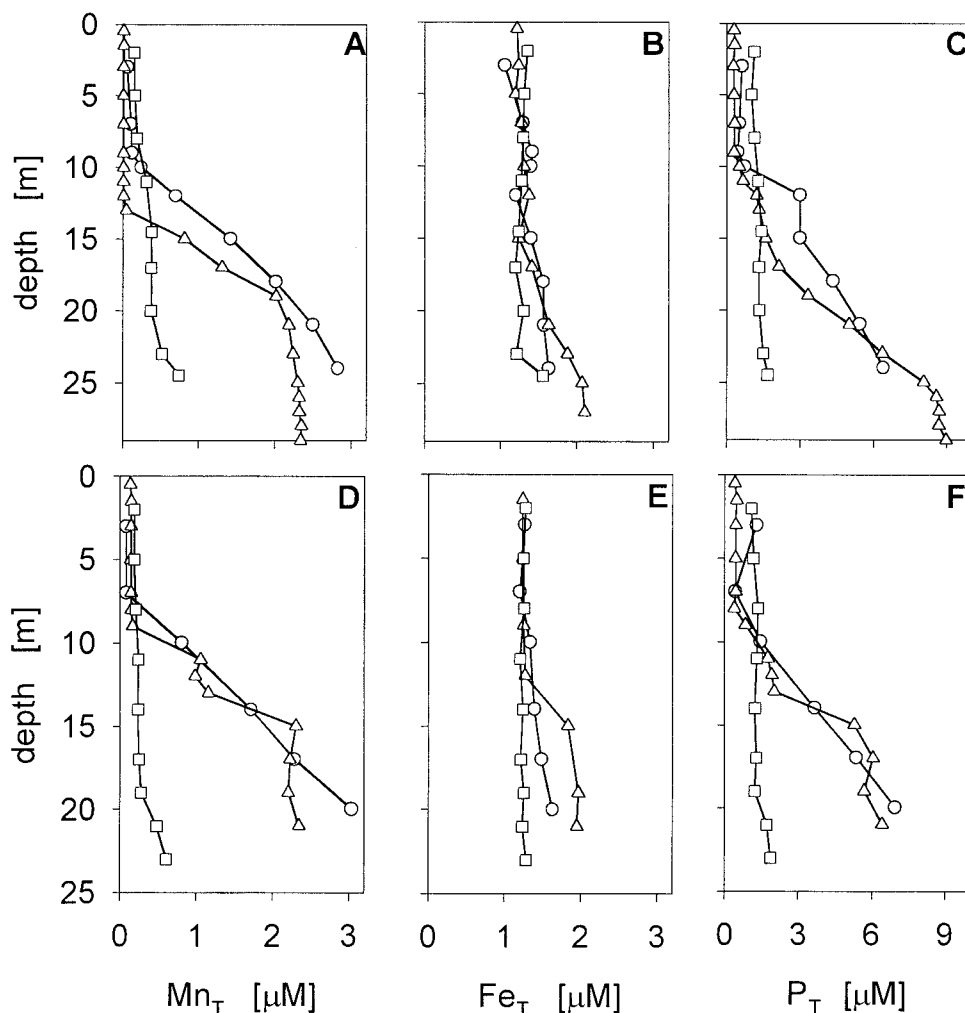


FIGURE 3. Total concentrations of manganese, iron, and phosphorus measured in water samples collected from Crowley Lake dam site (A–C) and basin site (D–F). Symbols: (○) August 4, 1998; (△) September 3, 1998; (□) May 11, 1999.

We estimate the volume of the hypolimnion to be $65 \times 10^6 \text{ m}^3$, calculated using a lake surface area of $21 \times 10^6 \text{ m}^2$ (ref 8 and references cited therein), defining the epilimnion as the upper 10 m based on our dissolved oxygen profiles, estimating the surface area of the hypolimnion from Figure 1, and approximating the cross-section of the hypolimnion as triangular with a maximum depth of 28 m, justified by the deep eastern channel created by the old Owens River bed. In the 3 weeks preceding the August sampling, only $1.7 \times 10^6 \text{ m}^3$ was withdrawn from the lake. However, between the August and September sampling dates, $30 \times 10^6 \text{ m}^3$, almost half the estimated volume of the hypolimnion, was withdrawn through the outlet at 21 m (20, 23). Storage was decreased by $5 \times 10^6 \text{ m}^3$ or only 3% of the total (24). The export of manganese associated with withdrawal of $30 \times 10^6 \text{ m}^3$ of water is $44 \times 10^3 \text{ mol}$, taking a volume-weighted manganese concentration within the hypolimnion. It is reasonable given the position of the outlet and the temperature (and associated density) gradient at the dam site to assume that all the exported water is withdrawn from the hypolimnion (25). Since the reservoir storage decreases by only $5 \times 10^6 \text{ m}^3$, at least $25 \times 10^6 \text{ m}^3$ of hypolimnetic water must be replenished by water originating from the epilimnion or surface inputs to the lake, which contain essentially no manganese. Thus, for the September profile to be the same as the August profile, the export of manganese and dilution with manganese-free water must be balanced by release of manganese from the sediments. If there had been no withdrawals, this release would have resulted in a volume-weighted average man-

ganese concentration in the hypolimnion in September of $2.3 \mu\text{M}$ as compared with the observed value of $1.4 \mu\text{M}$. In May, the manganese profiles show a very small increase of $\sim 0.3 \mu\text{M}$ (Figure 3A,D) near the sediment–water interface, suggesting that, even when the water column is well-oxygenated, the sediments are reducing.

Iron Profiles. The iron profiles are less pronounced than those of manganese during stratification (Figure 3B,E). A distinct signal of iron release from the sediments is apparent only in September. It is notable that significantly more manganese than iron is released into the water column during stratification even though the sediments contain more iron than manganese. In a 1991 sediment survey, the concentration of iron in the sediments was found to range from 4000 to 11 000 ppm with an average of 7000 ppm (7), values that are low relative to crustal abundance (56 300 ppm). Manganese ranged from 100 to 3000 ppm with an average of 600 ppm (7), values fairly comparable to crustal abundance (950 ppm). Reported sediment concentrations are consistent with the local geology, which consists primarily of basalt, rhyolite, and andesite (ref 1 and references cited therein). Bottom water samples collected in August and September smelled strongly of sulfide, and it is possible that iron is immobilized in the sediments as solid sulfide phases.

In contrast to the manganese concentrations in the hypolimnion, which stayed constant or even decreased slightly between August and September, the iron concentrations are slightly higher in September than in August. The September iron profiles show a signal of release from the

sediments that is not apparent in August. We hypothesize that the observed changes in the iron profiles may result from the introduction of oxygen associated with replacement of water withdrawn from the hypolimnion.

Although the surface water is well-oxygenated, the pronounced oxycline is maintained in September, which suggests that the newly introduced oxygen must be rapidly consumed in the hypolimnion. It is possible that this dissolved oxygen promotes oxidative dissolution of iron sulfide phases at the sediment–water interface and subsequent release of iron to the overlying water. The surface water iron concentrations are the same within experimental error at the two sites in September as are the bottom water iron concentrations, but at 15–20 m there is 40% more iron at the basin site than at the dam site, possibly an effect of the less dynamic flow regime at the basin site.

In August, only 70% of the total iron at the oxycline at the dam site passes a 0.45- μm filter as compared to 90% at the basin site. The precipitation of iron-containing solids above the oxycline at the dam site in August is corroborated by the presence of the black particulate material observed at this site.

Phosphorus—Uptake and Remineralization under Stratified Conditions. The phosphorus profiles under stratified conditions show significant enrichment at depth, consistent with the remineralization of algal biomass deposited on the lake floor (Figure 3C,F). Like manganese, phosphorus concentrations in the hypolimnion remain constant (or decrease slightly) between August and September. Again, only a substantial flux from the sediments could maintain these bottom water concentrations if the water withdrawn from the hypolimnion was replaced with surface water depleted in phosphorus. If the hypolimnetic water were replaced by water with elevated phosphorus concentration, then accumulation of phosphorus in the hypolimnion would have been observed despite the withdrawals.

The Owens River is enriched in phosphorus as a result of inputs from Big Springs, Hot Creek and possibly other sources (9). Phosphorus concentrations ranging from 4.2 to 8.1 μM with an average of 6.2 μM were measured at Benton Crossing (located 3 km north of Crowley Lake, below the confluence with Hot Creek) from January 1997 to October 1998 (19). The low phosphorus concentrations observed in the surface water of Crowley Lake in late summer (0.3–0.4 μM) can be attributed to algal uptake and dilution by other tributaries that are not subject to geothermal loading. The persistence of detectable phosphorus in the surface water in late summer suggests that phosphorus does not limit primary production in Crowley Lake.

In May, the concentration of phosphorus was uniform throughout the water column (Figure 3C,F) and somewhat higher than the surface water concentrations in August and September. Estimating the total phosphorus load in the water column suggests that less than 20% of the phosphorus present in September is removed by May, probably via withdrawal of the phosphorus-enriched hypolimnetic water before turnover.

Phosphorus concentrations in filtered and unfiltered samples were the same within experimental error at both sites during the summer with the exception of one sample collected at 3 m at the basin site in August, in which the phosphorus concentration in the filtered sample was 30% of that in the unfiltered sample. In May, phosphorus concentrations in filtered samples were 70–90% of those in the corresponding unfiltered samples.

Total Arsenic—No Evidence for Significant Sediment–Water Exchange. The total arsenic profiles in Crowley Lake exhibit three distinct patterns. In May, concentrations were uniform throughout the water column. In August, a minimum was observed at the oxycline, and in September, concentra-

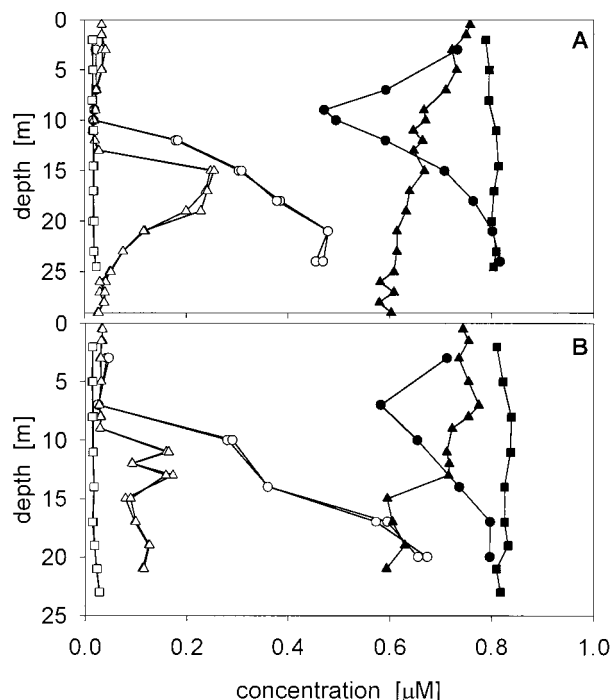


FIGURE 4. Concentrations of total arsenic (solid symbols) and arsenite (open symbols, duplicate field separations) measured in water samples collected from Crowley Lake dam site (A) and basin site (B). Symbols: (●, ○) August 4, 1998; (▲, △) September 3, 1998; (■, □) May 11, 1999.

tions decreased with depth (Figure 4). Arsenic concentrations in filtered and unfiltered samples were the same within experimental error. LADWP monitoring records show seasonal fluctuations in arsenic concentration at the dam outlet. The concentrations we measured are consistent with these records for August, September, and May over the years 1996–1999 (19).

The uniform concentrations measured in May are comparable to those measured in the deep water in August and the surface waters in August and September. A small (16%) loss of arsenic within Crowley Lake was indicated by a mass balance constructed in 1967 using historical, annually averaged input and withdrawal data (26). A mass balance for 1998 using monthly flow estimates for each of the tributaries (27), outlet flow data (20, 23), and arsenic concentrations measured monthly at Benton Crossing and Crowley Lake outlet (19) suggests that arsenic does not accumulate in Crowley Lake (22).

Neither the August nor the September arsenic profiles show evidence for substantial cycling of arsenic between the sediments and the water column, consistent with the mass balance calculation. Arsenic is not depleted in the surface waters, and concentrations at depth are not elevated compared to those at the surface. Arsenic is not associated with the particulate fraction in the water column, as evidenced by the indistinguishable arsenic concentrations in unfiltered and filtered samples.

The decrease in concentration with depth in September can be explained by replacement of water withdrawn from the hypolimnion by water with slightly lower total arsenic concentration. The surface inputs to the lake in August would have had lower arsenic concentration than the hypolimnetic water since the arsenic contributed by the Owens River, with 0.8 μM arsenic (19), was diluted approximately 1:1 in August by arsenic-free tributaries (27).

Minima in total arsenic concentrations were observed around the oxycline in August at both dam and basin sites. At the dam site, this profile is most likely due to adsorption

of arsenic onto the black precipitate observed in these samples (vide supra). The concentration increase below this minimum may be due to release of arsenic, by reductive dissolution, from the rapidly settling particles formed at the oxycline. Thus, the shape of the August profile can be attributed to internal cycling of arsenic *within the water column* rather than to release of arsenic from the sediment. This pattern is also observed but is much less pronounced at the basin site, which is likely to be more representative of the lake as a whole.

The mass flux of arsenic through Crowley Lake is approximately 15×10^3 kg/yr. Thus, even removal from the water column, which would be insufficient to perturb the vertical profiles of arsenic, could result in moderate accumulation of arsenic in the sediments. Arsenic concentrations in Crowley Lake sediments surveyed in 1991 ranged from near-background values of 4–80 ppm (dry wt) (7). Arsenic concentrations in surface sediments we collected in July 1999 were 140 ppm at the basin site and 260 ppm at the dam site (on a dry wt basis, determined by X-ray fluorescence). It appears, on the basis of X-ray absorption spectroscopy, that arsenic is immobilized in these sediments as a sulfide solid (22).

Arsenite Speciation. Arsenite concentrations in August increased with depth below the oxycline (Figure 4). At the dam site, the increase in arsenite parallels the increase in total arsenic, which we have attributed to internal recycling in the water column. At the basin site, the increase in arsenite is substantially greater than the increase in total arsenic and thus reflects reduction of arsenate.

The unusual arsenite profiles observed in September were most likely due to the large outflow from the reservoir prior to sample collection (Figure 4). Arsenite produced in the deep waters prior to the August sampling is withdrawn, being replaced by arsenate-bearing surface waters. The basin site is considerably further from the outlet than the dam site, and this may account for the difference between the two sites. These results highlight the impact that reservoir operations can have on the distribution of redox-active chemical species.

In the well-mixed conditions in May, arsenite was not an important species at any depth in the water column (Figure 4).

Organic arsenic species did not contribute significantly to the total arsenic concentrations in any samples collected. In the productive, summer months, more than 95% of the arsenic in the epilimnion was present as arsenate. Since DMA, if present, would have eluted with arsenite in the on-site sample processing, the small amount of arsenic in this fraction (Figure 4) implies that DMA is not a significant species in the epilimnion. The IC–ICPMS method revealed no MMA in any of the samples analyzed. Thus, although the surface waters were very productive, these methylated species were not abundant.

Implications for Water Quality in the Los Angeles Aqueduct. Two common mechanisms that facilitate transport of arsenic from the water column to the sediment in freshwater lakes are adsorption to oxyhydroxides and uptake by phytoplankton. In Crowley Lake, however, these mechanisms do not appear to be effective in depositing arsenic to the sediments. Crowley Lake receives large inputs of geothermal phosphorus, which may displace arsenate from the phytoplankton cycle. Phosphate would also compete with arsenic for sorption sites on iron and manganese oxyhydroxides, although the Crowley Lake system is relatively poor in these metals.

Arsenic is moderately elevated in the Crowley Lake sediments and is associated with a sulfide phase that should be stable when the sediment–water interface is anoxic. The decrease in dissolved oxygen and the increase in manganese

concentrations at depth in May suggest that the sediments are permanently reducing. Release of arsenic from the sediments was not observed in Crowley Lake under either stratified or unstratified conditions. Thus, if upstream water was treated to remove arsenic, it is unlikely that the release of arsenic from Crowley Lake sediments would substantially degrade the quality of the LAA water supply.

Acknowledgments

We thank F. Bohn, D. Giammar, T. Piatina, and J. Stephens for assistance with sample collection; D. Ball, C. Bagaous, J. Biedelman, D. Christie, S. Keef, and G. Stolarik of the Los Angeles Department of Water and Power for providing information and monitoring records; and the staff at the Crowley Lake Fish Camp for providing the data for Figure 1. The work was supported by the U.S. Environmental Protection Agency (826202-01-0).

Literature Cited

- (1) Eccles, L. A. *Water-Resour. Invest. (U.S. Geol. Surv.)* **1976**, No. 76-36.
- (2) U.S. EPA. Proposed Revision to Arsenic Drinking Water Standard, 2000, <http://www.epa.gov/safewater/ars/proposals.html>.
- (3) Stolarik, G. F.; Christie, J. D. *Proceedings of the 1999 American Water Works Association Annual Conference*, Chicago, IL, June 20–24, 1999.
- (4) Seyler, P.; Martin, J. *Environ. Sci. Technol.* **1989**, 23 (10), 1285–1263.
- (5) Anderson, L. C. D.; Bruland, K. W. *Environ. Sci. Technol.* **1991**, 25 (3), 420–427.
- (6) Kuhn, A.; Sigg, L. *Limnol. Oceanogr.* **1993**, 38 (5), 1052–1059.
- (7) SWRCB. *Mono Basin EIR Auxiliary Report No. 17*; California State Water Resources Control Board: 1993.
- (8) U.S. EPA National Eutrophication Survey. *Working Paper 743*; U.S. Environmental Protection Agency: Washington, DC, 1978.
- (9) Melack, J. M.; Lesack, L. F. W. Long Valley Reservoir Research Program, Progress Report. Department of Biological Sciences and Marine Science Institute, University of California, Santa Barbara, CA, 1982.
- (10) Aurilio, A. C.; Mason, R. P.; Hemond, H. F. *Environ. Sci. Technol.* **1994**, 28 (4), 577–585.
- (11) Sohrin, Y.; Matsui, M.; Kawashima, M.; Hojo, M.; Hasegawa, H. *Environ. Sci. Technol.* **1997**, 3 (10), 2712–2720.
- (12) Andrae, M. O. *Limnol. Oceanogr.* **1979**, 24 (3), 440–452.
- (13) Sanders, J. G.; Windom, H. L. *Estuarine Coastal Mar. Sci.* **1980**, 10, 555–567.
- (14) Aggett, J.; O'Brien, G. A. *Environ. Sci. Technol.* **1985**, 19 (3), 231–238.
- (15) Aggett, J.; Kriegman, M. R. *Water Res.* **1988**, 22 (4), 407–411.
- (16) Moore, J. N.; Ficklin, W. H.; Johns, C. *Environ. Sci. Technol.* **1989**, 22 (4), 432–437.
- (17) Azcue, J. M.; Nriagu, J. O.; Schiff, S. *Environ. Int.* **1994**, 20 (4), 517–527.
- (18) Freeman, M. C.; Aggett, J.; O'Brien, G. *Water Res.* **1986**, 20 (3), 283–294.
- (19) Ball, D. A. Los Angeles Department of Water and Power, personal communication, 1998.
- (20) Bagaous, C. L. Los Angeles Department of Water and Power, personal communication, 1999.
- (21) Wilkie, J. A.; Hering, J. G. *Environ. Sci. Technol.* **1998**, 32 (5), 657–662.
- (22) Kneebone, P. E. Ph.D. Dissertation, California Institute of Technology, 2000.
- (23) Biedelman, G. J. Los Angeles Department of Water and Power, personal communication, 1998.
- (24) California Data Exchange Center. 2000, <http://cdcewater.ca.gov>.
- (25) Brooks, N. H.; Koh, R. C. Y. *J. Hydraul. Div., ACSE* **1969**, 95 (HY4), Proc. Paper 6702, 1369–1400.
- (26) DWR. *Investigation of Geothermal Waters in the Long Valley Area, Mono County*; State of California Department of Water Resources: 1967.
- (27) Keef, S. Los Angeles Department of Water and Power, personal communication, 1999.

Received for review January 21, 2000. Revised manuscript received July 21, 2000. Accepted July 21, 2000.

ES000923U